OPEN ACCESS

Volume: 6

Issue: 4

Month: April

Year: 2019

ISSN: 2321-788X

Received: 16.03.2019

Accepted: 30.03.2019

Published: 02.04.2019

Citation:
Raja, K. “Reaction of Sodium Nitroprusside and Potassium Dichromate on Benzaldehyde Di N-Butyl Acetal.” *Shanlax International Journal of Arts, Science and Humanities*, vol. 6, no. 4, 2019, pp. 43–46.

DOI:
https://doi.org/10.34293/sijash.v6i4.369

Reaction of Sodium Nitroprusside and Potassium Dichromate on Benzaldehyde Di N-Butyl Acetal

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Abstract
There action of benzaldehyde di n-butylacetal catalyzed by halomethanes in contrast to those catalyzed by Lewis acids, n-halocompounds, etc., has received only a little attention. Aliphatic acetal gives benzaldehyde and butyl benzoate as the main products. This reaction features induced the authors to take up the title investigations. Halomethanes are synthetically very useful reagents and vary widely in their acceptor synthon character and reactivity, hence their applications in the present work.

Keywords: Benzaldehyde di n-butylacetal, Sodium Nitroprusside, Potassium Dichromate and Acetonitrile

Introduction

Alphonse has investigated the action of various Lewis acids on aromatic acetals and proposed mechanism based on carbocation intermediate. The reactions of aliphatic acetals catalyzed by solid acids have been extensively studied by various researchers and in most cases synthetically important α, β-unsaturated ethers have been obtained as the major products. The unsaturated ether was shown to be formed by the elimination of alkoxy group and the removal of a proton from the β-carbon of acetal.

The elimination may occur either in a concerted or stepwise manner depending on the nature of the catalyst.

Xavier and Arul raj have reported that when aromatic acetals in vapour phase were passed over gamma alumina, the product mixture was found to contain ester, ether and aldehyde of aromatic nature.

The reactions of aliphatic acetals catalysis by solid acids have been extensively studied by various researchers and in most cases synthetically important αβ -unsaturated ethers have been obtained as major products. Klein (1954) got a good yield of alkyl vinyl ether by passing aliphatic acetal over barium oxide on silica get at elevated temperatures Ilagemayar and Perry (1957) obtained aldehyde as one of the major products in the study of aliphatic acetals catalyzed by alumina .In 1967, Michitoshi et al. Found out that metal sulphates supported on γ-alumina could act as an effective catalyst for the formation of ethyl vinyl ether from acetaldehyde diethyl acetal. They suggested acid catalyzed mechanism for the reaction and ruled out the thermal decomposition of acetal under their experimental conditions.

Makin et al in (1976) obtained the corresponding unsaturated ether during their study on cyclohexane acetal over ammonium dihydrogen phosphate. Similarly on sodium hydrogen sulphate catalyst Cobum (1977) got 92 percent unsaturated ether from nitro substituted acetal.

Studies made by Angayal and James have shown that acetals are not as very resistant to oxidative cleavage as is generally believed to be Oxidations of acetals by different reagents have been carried out. They have shown that chromium trioxide in acetic acid oxidizes acetals R1CH(OR2)(OR3) and aldehydes to esters, R1COOR2 in which one of the alkoxy groups constituting the acetal has been retained while the other is usually oxidized to a ketone. These authors have found that glycosides being acetals are oxidized according to the general scheme, the glycon being retained and the ring being ruptured.

Kinetic study of oxidation of acetals and substituted aromatic acetals by chromic acid in aqueous acetic medium yielded the corresponding esters as the main product.

Electrochemical oxidative studies on aromatic acetals in acetonitrile medium have been reported by Krishnamurthy and Arulraj Under electrical field, with the help of a radical obtained from a supporting electrolyte, acetals were found to yield esters.

Dichlorine monoxide, a powerful and selective chlorinating agent has been used for either side chain or chlorination of deactivated aromatic substrates and it gives excellent yields under mild conditions.

The electrophile produced from Cl2O and strong acids has limited stability at room temperature and has been characterized.

The chlorination of anisole by hypochlorous acid has been studied in which the chloronium ion, Cl+ is the attacking species. The intermediate found is a sigma complex.

Many N-halocompounds are used as important reagents in organic chemistry. The N-halocompounds such as N-chlorosuccinimide, N-chloronaphthalimide, N-chlorosaccharin, N-chloropiperidone have already been used in the oxidation reactions. The study of kinetics involving N-halo compounds has led to the mechanism of their action.

Materials

Substrate: The benzaldehyde di n-butyl acetal was prepare and its purity was checked by TLC (Thin Layer Chromatography)

Solvent: Acetonitrile was purify by standard distillation and used as the solvent.

Reagents: Nice samples of Sodium Nitroprusside, Potassium Dichromate, were bought and used for the reactions.

Experimental Section

1. Acetal Preparation

Benzaldehyde di n-butylacetal : 100ml of freshly vacuum distilled benzaldehyde, and 200ml of distilled n-butyl alcohol were taken in a 500ml round-bottomed flask fitted with a Dean-Stark apparatus carrying a reflux condenser attached to a calcium chloride guard tube. 8g of calcium chloride and 100 ml of pure dry benzene were add and the mixture was reflux for 8 hours.The flask was cooled to room temperature, and the contents were poured into a separating funnel. The solution was wash with water. The solution was dry over anhydrous sodium sulfate.

The unreacted alcohol and benzene were remove by atmospheric distillation. The remaining mixture was distill under reduced pressure. Pure acetal was collect at 196oC-200oC.

2. An action of Sodium Nitroprusside on benzaldehyde di n-butylacetal

a) A reaction of Sodium Nitroprusside with benzaldehyde di n-butylacetal

5 ml of benzaldehyde di-n-butylacetal dissolved in 10 ml of acetonitrile was taken in a 250 ml conical flask, 6.65 g of sodium nitroprusside was dissolved in 10 ml of water and was added drop wise to the same flask, fitted with a magnetic stirrer. The reaction mixture was stirred and the stirring was continued for half an hour. The reaction mixture was washed with water and the product was extracted with diethyl ether. The resulting reaction mixture was spotted at the TLC. The product was separated by column chromatography and analysed by IR spectrum.

3. An action of Potassium Dichromate on benzaldehyde di n-butylacetal

a) An action of Potassium Dichromate with benzaldehyde di n-butylacetal

5 ml of benzaldehyde di-n-butylacetal dissolved in 10 ml of acetonitrile was taken in a 250 ml conical flask, 7.4 g of potassium dichromate was dissolved in

10 ml of water and was added drop wise to the same flask, fitted with a magnetic stirrer. The reaction mixture was stirred and the stirring was continued for half an hour. The reaction mixture was washed with water and the product was extracted with diethyl ether. The resulting reaction mixture was spotted at the TLC. The product was separated by column chromatography and analysed by IR spectrum.

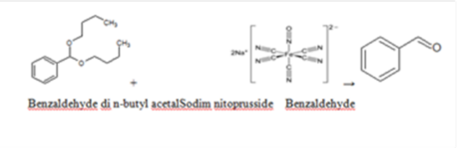
Results and Discussion

An action of Sodium Nitroprusside and Potassium Dichromate on benzaldehyde di n-butylacetal

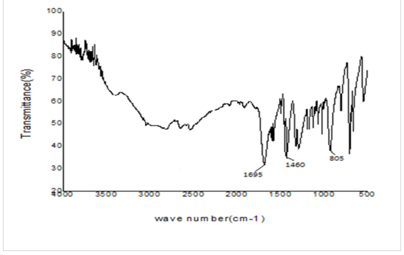
The acetal contains the benzal carbonatom which is surrounded by one H atom and the other three bulky groups namely benzene ring and the two butoxy groups.Thus the acetal requires steric relief. Thus the butoxy oxygen atom with two lone pairs is longing to attack any acceptor synthon.This is the driving force for the attack of the alkoxy oxygen on the acceptor synthon.

The action of SodiumNitroprusside and Potassium Dichromate on the benzaldehyde di n-butylacetal gave the corresponding benzaldehyde and butyl benzoate respectively. Sodium Nitroprusside and Potassium Dichromate, Sodium are inorganic salts which are ready to draw nucleophile towards it since the chosen inorganic salts are having electron withdrawing inductive effect thus the acetal makes use of its lone pair on the alkoxy oxygen and forms oxonium ion. AnR group isundergoes steric hindrance and, the R group is the driving force for the R to get cleaved as RH abstracting the methine H atom. Thus the intermediate is results. The reagent Sodium Nitroprusside and Potassium Dichromate, which has acted as the catalyst are relieved when the benzaldehyde and butyl benzoate is formed as the products.

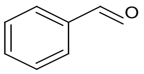
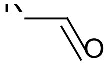
Mechanism: 1



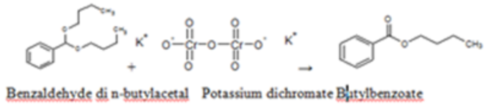
IR Spectrum of Benzaldehyde



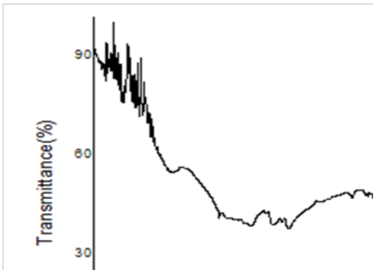
Spectral Characterisation of Benzaldehyde

Structure	FTIR in cm-1	Characteristic functional group
	1685-1710	

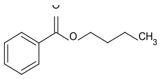
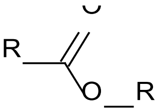
Mechanism 2



IR Spectrum of Butylbenzoate



Spectral Characterisation of Butylbenzoate

Structure	FTIR - in cm-1	Characteristic functional Group
	1250-1310	

Conclusion

The reactions of the benzaldehyde di n-butylacetal with Sodium Nitroprusside and Potassium Dichromate were studied at room temperature.

The reagents Sodium Nitroprusside and Potassium Dichromate were found to yield the products benzaldehyde and butyl benzoate respectively. The formation of benzaldehyde and butyl benzoate are explained by the IR spectra. The Presence of cl is confirmed by the confirmatory element test. Just as the Sodium Nitroprusside and Potassium Dichromate many more acceptor synthons can be used to react with the acetals and such reactions can be run.

Many more aromatic nuclei like furan, pyrrole, thiophene, pyridine, etc. other than the benzene nucleus can be used in the synthesis of the acetals. The same reagents used in the present study can also be treat with aliphatic acetals, heteroaromatic acetals with different hetero atoms such as N, S, and O.

The same reactions can be carried out even at a high temperature (or) at low temperature. Variety of alcohols can be used to synthesize the different acetals excluding what has reported in the present study. Many more solvents can be try out other than acetonitrile.

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